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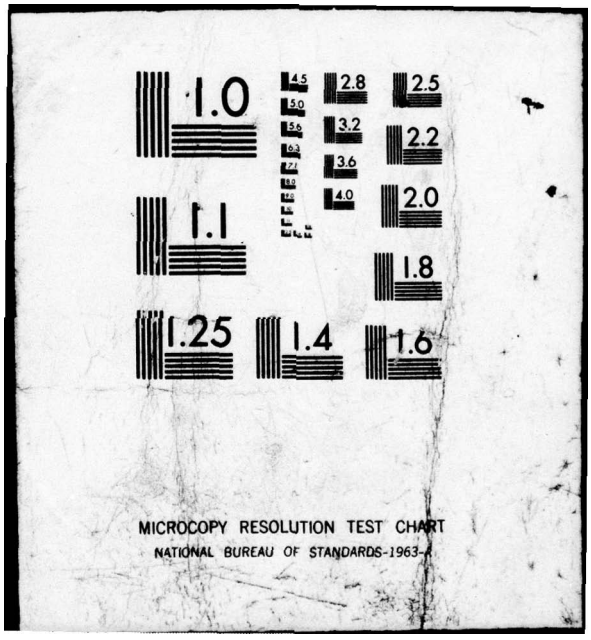
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January 1977

Report No. ONR 1-6
(Annual)

HIGH ENERGY HALOGEN CHEMISTRY

by

K. Baum, J. S. Horn and D. A. Lerdal

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Fluorodinitroalkyl silicones
Nitration
Fluorination
Polymerization
Phosphazenes
Nuclear magnetic resonance spectra
Infrared spectra

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(3-Fluoro-3,3-dinitropropyl)methyldiphenylsilane was prepared from (3-bromopropyl)methyldiphenylsilane by sodium nitrite displacement, oxidative nitration and fluorination. Reaction with bromine gave (3-fluoro-3,3-dinitropropyl)methyldibromosilane. The dibromide was hydrolyzed under a variety of condition to give cyclic polysiloxanes. The dibromide or the polysiloxanes reacted with HF to give (3-fluoro-3,3-dinitropropyl)methyldifluorosilane, which was hydrolyzed readily by base but was relatively stable to aqueous

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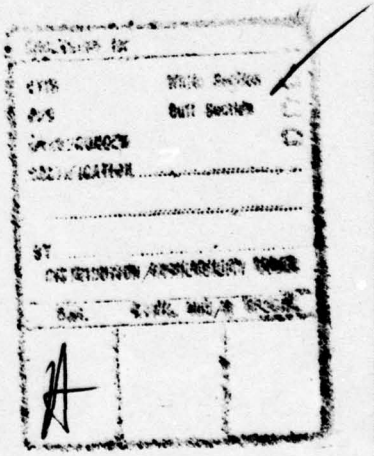
20. ABSTRACT (cont'd.)

acid. Polymerization of the cyclic polysiloxanes was studied. By a synthesis sequence similar to that above, bis-2(3-fluoro-3,3-dinitropropyl(diphenylsilane was prepared. Brominative dephenylation and hydrolysis gave the cyclic trisiloxane. The reaction of fluorodinitroethanol with poly(dichlorophosphazine) in pyridine gave replacement of chlorines by fluorodinitroethoxy groups, but considerable amounts of pyridine were also incorporated into the polymer.



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I. INTRODUCTION

The objective of this research program is to synthesize new functional groupings with potential utility in high energy propellants and explosives. During the past year, the major emphasis of this research has been the synthesis of energetic examples of silicones, a class of polymers generally recognized to have exceptional low temperature flexibility as well as high thermal stability. The general synthetic procedures developed in the preceding report period for introducing nitro and fluorine groups into silane molecules were extended to polysiloxanes. Process improvement and scale up studies were made to enable the preparation of sufficient materials for polymerization studies. Some exploratory work was also done in the area of fluorodinitro substituted polyphosphazenes.

II. DISCUSSION

In the preceding report[1] exploratory studies in the area of fluorodinitroalkyl silicon chemistry were described. Work with model trimethylsilyl derivatives showed that fluorodinitroalkyl groups attached to silicon can be prepared by nitrite displacement of halogen, oxidative nitration and fluorination, i.e.:

$$(CH_3)_3SiCH_2CH_2CH_2Br \xrightarrow{NaNO_2} (CH_3)_3SiCH_2CH_2CH_2NO_2 \xrightarrow[NaNO_2,\ OH^-]{AgNO_3} (CH_3)_3SiCH_2CH_2CH(NO_2)_2 \xrightarrow[F_2]{OH^-}$$

$$(CH_3)_3SiCH_2CH_2CF(NO_2)_2$$

In the application of this sequence to the preparation of a nitropolysiloxane, the phenyl group was applied as a silicon blocking agent. Thus, (3-bromopropyl)-methyldiphenylsilane was converted in a similar way to the fluorodinitro analog. Treatment of this compound with bromine removed the phenyl groups selectively and gave the dibromosilane. Hydrolysis then gave a mixture of cyclic oligomers.

$$(C_6H_5)_2CH_3SiCH_2CH_2CH_2Br \longrightarrow \longrightarrow (C_6H_5)_2CH_3SiCH_2CH_2CH(NO_2)_2$$

$$\xrightarrow[FClO_3]{OH^-} (C_6H_5)_2CH_3SiCH_2CH_2CF(NO_2)_2 \xrightarrow{Br_2}$$

$$Br_2CH_3SiCH_2CH_2CF(NO_2)_2 \xrightarrow{H_2O} (-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_2CF(NO_2)_2}{\overset{|}{\underset{|}{Si}}}}-O-)_n \qquad n = 3\text{-}5$$

Work had also been initiated on the difunctional analog and $(C_6H_5)_2Si(CH_2CH_2CH_2NO_2)_2$ was obtained.

The objective of this work has been to utilize the excellent low temperature flexibility and high thermal stability generally associated with silicones in high energy systems. Low to moderate molecular weight polysiloxanes and silanes

are potentially useful as plasticizers, and high molecular weight polysiloxanes, as binders for propellants and explosives. Rubbery polymers are of particular interest because of the paucity of available energetic examples. To obtain sufficient materials for polymerization efforts, scale-up and process improvement studies were needed.

Monomer Synthesis. Previously, the starting material, (3-bromopropyl)methyldiphenylsilane, was obtained by the following route:

$$CH_3(C_6H_5)_2SiH + CH_2{=}CHCH_2OCOCH_3 \longrightarrow CH_3(C_6H_5)_2SiCH_2CH_2CH_2OCOCH_3$$

$$\xrightarrow[H_2O]{NaOH} CH_3(C_6H_5)_2SiCH_2CH_2CH_2OH \xrightarrow[C_5H_5N]{CH_3C_6H_4SO_2Cl}$$

$$CH_3(C_6H_5)_2SiCH_2CH_2CH_2OSO_2C_6H_4CH_3 \xrightarrow[DMSO]{LiBr}$$

$$CH_3(C_6H_5)_2SiCH_2CH_2CH_2Br$$

The addition of diphenylmethylsilane to allyl acetate, catalyzed by chloroplatinic acid, was repeated three times. The ester was not isolated but was hydrolyzed directly to the alcohol. The scale was increased to give 330 g of alcohol (46% yield) but a 100% excess of allyl acetate was needed. Improvements in the procedure were made by substituting allyloxytrimethylsilane ($CH_2{=}CHCH_2OSi(CH_3)_3$) for allyl acetate, and, subsequently, chlorotris(triphenylphosphine)rhodium for chloroplatinic acid as the catalyst (see Table 1). Thus, the silyl ether in 10% excess gave a 71% yield of alcohol with chloroplatinic acid. A 15% excess of the silyl ether with the rhodium catalyst gave essentially a quantitative yield of the alcohol. The reaction was scaled up to yield about

Table 1. Reactions of $(C_6H_5)_2CH_3SiH$ with $CH_2=CHCH_2OOCCH_3$ and with $CH_2=CHCH_2OSi(CH_3)_3$

Run No.	Moles $(C_6H_5)_2CH_3SiH$	Moles $CH_2=CH-CH_2OX$ CH_3CO_2-	Moles $CH_2=CH-CH_2OX$ $(CH_3)_3Si-$	Catalyst	Temp °C	Yield $(C_6H_5)_2MeSiCH_2CH_2CH_2OH$ g	Yield (moles)	Yield %
1	1.0	2.0	-	H_2PtCl_6	105°	125	(0.49)	49
2	1.0	2.0	-	"	"	120	(0.47)	47
3	2.8	5.6	-	"	"	330	(1.3)	46
4	0.41	-	0.41	"	115°	66	(0.26)	63
5	0.98	-	1.1	"	100°	177	(0.69)	71
6	1.0	-	1.0	$[(C_6H_5)_3P]_3RhCl$	95-150°	203	(0.79)	79
7	5.0	-	5.0	"	120-130°	1013	(3.96)	79
8	5.0	-	5.75	"	130°	1123	(4.39)	88
9	"	-	"	"	"	1255	(4.90)	98
10	"	-	"	"	"	1149	(4.49)	90
11	"	-	"	"	"	1200	(4.69)	94
12	"	-	"	"	"	1255	(4.90)	98
13	7.77		8.94	"	"	1950	(7.62)	98

2 kg of the alcohol. The $CH_2=CHCH_2OSi(CH_3)_3$ was prepared in kilogram quantities by the reaction of allyl alcohol with chlorotrimethylsilane (Table 2).

The alcohol was converted to the toluenesulfonate by reacting it with a slight excess of toluenesulfonyl chloride and pyridine in methylene chloride solution. Yields were generally in the range of 60-70% (Table 3). Run 12 represents an attempt to utilize the mother liquors from cyrstallization of product, which were found by NMR to contain the alcohol. Reacting this crude material with toluenesulfonyl chloride gave a 46% yield of product, somewhat less pure than usual. The early runs were carried out at low temperatures, but similar results were obtained at ambient temperature.

The substitution of the toluenesulfonate by bromide was carried out in dimethyl sulfoxide, using sodium bromide rather than the more expensive lithium salt used previously. NMR showed that the yield of bromide was quantitative, and since the next step is carried out in the same solvent, the bromide was not isolated. Sodium nitrite was added, and the course of the reaction was followed by NMR. The experiments are summarized in Table 4. The major byproduct is the nitrite, $(C_6H_5)_2CH_3SiCH_2CH_2CH_2ONO$, but the alcohol, $(C_6H_5)_2CH_3SiCH_2CH_2CH_2OH$, is also formed. Overlapping NMR peaks prevent resolution of the latter from the starting bromide, so totals are given. In runs 2-5 and 7-9, the crude mixture was used directly in the subsequent oxidative nitration step. In the other runs, the nitro compound was purified by extracting the crude mixture with base and precipitating the nitro compound by acidifying the aqueous solution. The last column of Table 4 shows the NMR based yields in this still somewhat impure material. The nitrite displacent is exothermic, and the reaction temperature was generally kept below 35° with a cooling bath. In runs 9, 10 and 20,

Table 2. Allyloxytrimethylsilane

Run No.	Moles CH_2=CH-CH_2OH	Moles $(CH_3)_3SiCl$	Yield g	CH_2=CH-$CH_2OSi(CH_3)_3$ (moles)	%
1	1	1	53	(0.41)	41
2	2	2	140	(1.08)	54
3	2	2	137	(1.06)	53
4	6	6	520	(4.0)	67
5	24	24	2390	(18.4)	77
6	54	54	4543	(34.9)	65

Table 3. 3-(p-Toluenesulfonatopropyl)methyldiphenylsilane

Run No.	Moles $(C_6H_5)_2MeSi(CH_2)_3OH$	Moles Toluenesulfonyl Chloride	Moles Pyridine	Temp	Time	Yield $(C_6H_5)_2MeSi(CH_2)_3OTs$ g	(Moles)	%
1	0.38	0.42	0.42	4°	3 days	60	(0.15)	53
2	1.61	1.77	1.77	-16°	3 days	472	(1.15)	72
3	0.30	0.33	0.33	-16°	20 hrs	61	(0.15)	50
4	0.26	0.28	0.28	-16°	20 hrs	69	(0.17)	65
5	0.26	0.28	0.28	-16°	20 hrs	35	(0.085)	33
6	0.69	0.76	0.76	-16°	20 hrs	167	(0.41)	59
7	0.79	0.87	0.99	20°	20 hrs	198	(0.48)	61
8	3.96	4.35	4.95	"	"	1037	(2.53)	64
9	4.39	4.83	5.49	"	"	1049	(2.56)	58
10	5.0	5.5	6.25	"	"	1173	(2.86)	57
11	4.49	4.94	5.61	"	"	1112	(2.71)	60
12	3.54	3.54	7.0	"	"	665	(1.62)	46
13	4.67	5.14	5.84	"	"	1312	(3.20)	69
14	4.90	5.39	6.12	"	"	1262	(3.08)	63
15	7.62	8.38	9.52	"	"	1925	(4.70)	62

Table 4. Conversion of $(C_6H_5)_2CH_3SiCH_2CSO_2C_7H_7$ to $(C_6H_5)_2CH_3SiCH_2CH_2CH_2NO_2$

Run No.	Moles Toluenesulfonate	NMR Ratios Nitrite	Alcohol-Bromide	(%) Nitro	NMR Yield Nitro g	%	NMR Yield Purified Nitro g	%
1	0.122	28	9	63	-		-	
2	1.15	21	29	50	165	(50)	-	
3	1.28	30	9	60	197	(54)	-	
4	2.53	30	15	55	402	(56)	-	
5	5.42	23	25	53	502	(45)	-	
6	1.62	18	26	56	167	(36)	37	(8)*
7	1.36	23	18	59	200	(52)	-	
8	1.36	18	23	59	175	(45)	-	
9	1.0	-	69	31	48	(17)*		
10	1.0	-	67	33	-	- *	-	
11	0.25	22	28	50	33	(46)	24	(34)
12	0.25	18	26	56	33	(46)	25	(35)
13	1.26	23	22	55	-	(48)	111	(31)
14	1.0	21	26	53	-	-	87	(31)
15	1.0	-	-	-	-	-	99	(35)
16	1.0	-	-	-	-	-	75	(26)
17	1.0	-	-	-	-	-	95	(33)
18	1.0	-	-	-	-	-	131	(46)
19	1.0	-	-	-	-	-	94	(33)
20	1.2	-	-	-	-	-	56	(16)

*overheated reaction

the temperature was allowed to rise to about 60°, and low yields resulted. In run 6, an attempt was made to remove the solvent at atmospheric pressure rather than vacuum, and again the high temperature resulted in product decomposition. On a large scale, the alcohol could be recycled, and the nitrite could be hydrolyzed easily to the alcohol.

The oxidative nitration experiments, converting the nitro compound to the corresponding gem-dinitro compound, are summarized in Table 5. Runs 1-4 were made using the unpurified mixture from the nitrite displacement reaction. The mixtures were extracted with the theoretical amount of base determined by the nitro content, and the aqueous solution was treated with silver nitrate and sodium nitrite. In runs 5-15 the purified nitro compound described above was used. In runs 6-15, a change in the reaction solvent was made. The addition of methanol gave a more easily filterable silver precipitate, and yields of dinitro compound as high as 79% were obtained.

Fluorinations of the potassium salt of the dinitro compound were carried out with perchloryl fluoride in methanol in as high as 85% yield (Table 6). The previously reported procedure[1] was used. Variations in yields may be reflections of starting material quality, since the intermediates between this product and the toluenesulfonate were not crystallized or distilled. The fluorination product was obtained in pure form by column chromatography on silica gel.

Conversion of $(C_6H_5)_2CH_3SiCH_2CH_2CF(NO_2)_2$ to $Br_2CH_3SiCH_2CH_2CF(NO_2)_2$ was carried out by heating with bromine at 100°, as reported previously.[1] The product was distilled, and yields were as high as 74% (Table 7). Run 3 represents an attempt to debrominate crude diphenyl compound that was not purified by chromatography.

Table 5. Oxidative nitration

Run No.	Moles $(C_6H_5)_2CH_3SiCH_2CH_2CH_2NO_2$	Solvent	NMR Yield $(C_6H_5)_2CH_3SiCH_2CH_2CH(NO_2)_2$ g	(moles)	%
1	0.075	H_2O,Et_2O	12.7	(0.038)	51
2	0.69	"	73	(0.22)	32
3	1.41	"	209	(0.63)	45
4	0.70	"	69	(0.21)	30
5	0.61	"	81	(0.25)	40
6	0.084	MeOH,H_2O,Et_2O	22	(0.067)	79
7	0.088	"	16	(0.048)	55
8	0.077	"	17	(0.052)	68
9	0.31	"	64	(0.19)	62
10	0.31	"	63	(0.19)	62
11	0.35	"	89	(0.27)	77
12	0.26	"	57	(0.17)	66
13	0.33	"	85	(0.26)	77
14	0.46	"	104	(0.32)	69
15	0.33	"	64	(0.19)	59

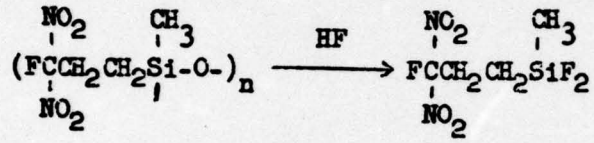
Table 6. (3-Fluoro-3,3-dinitropropyl)methyldiphenylsilane

Run No.	Moles $(C_6H_5)_2CH_3SiCH_2CH_2CH(NO_2)_2$	Yield $(C_6H_5)_2CH_3SiCH_2CH_2CF(NO_2)_2$ g	(moles)	%
1	0.038	11	(0.032)	85
2	0.22	44	(0.12)	57
3	0.63	111	(0.32)	51
4	0.45	92	(0.26)	58
5	0.77	191	(0.55)	70
6	0.50	115	(0.35)	65
7	0.50	100	(0.30)	57

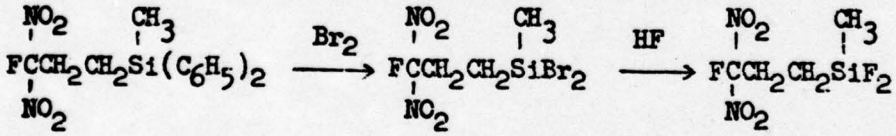
Table 7. (3-Fluoro-3,3-dinitropropyl)methyldibromosilane

Run No.	Moles $(C_6H_5)_2CH_3SiCH_2CH_2CF(NO_2)_2$	Yield $Br_2CH_3SiCH_2CH_2CF(NO_2)_2$ g	(moles)	%
1	0.032	6.9	(0.019)	61
2	0.125	31	(0.088)	70
3	0.1 crude	7	(0.020)	18
4	0.26	57	(0.16)	60
5	0.32	83	(0.23)	74
6	0.29	72	(0.20)	71

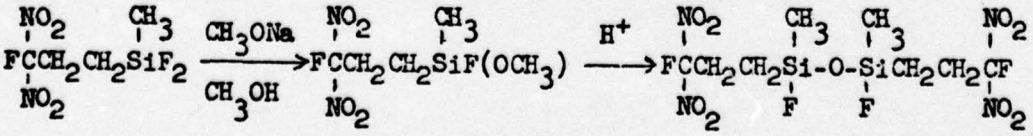
Difluorosilanes are generally hydrolyzed much more slowly than dibromosilanes or dichlorosilanes under neutral or acidic conditions, although all are hydrolyzed rapidly under alkaline conditions. The synthesis of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane was therefore undertaken as a monomer with selective reactivity. The compound was obtained in 80% yield by the reaction of HF in ethanol with polysiloxanes resulting from the hydrolysis of the dibromide. This method is of particular value in providing useful products from unreactive oligomer fractions, described below.



The difluoride was also obtained in 82% yield by the reaction of the dibromide with NaF and HF in ethanol. It was found that it was not necessary to purify the dibromide used as a starting material for this displacement. Addition of HF to the crude material resulting from dephenylation gave the difluoride a readily distillable liquid.



The inertness of silicon fluorides toward acids was utilized to prepare the dimeric fluoride. Thus, the difluoride reacted with sodium methoxide in methanol to give the methoxy fluoride. This methoxy group was cleaved by aqueous acid, whereas the fluoride was stable, yielding the dimer:



In the preceding report[1] several routes to the analogous silane system with two fluorodinitropropyl groups were described. The most practical route is shown in the following reaction sequence, and enough of the nitrite substitution product was obtained for identification. This work was continued.

$$(C_6H_5)_2SiH_2 + CH_2{=}CHCH_2OOCCH_3 \xrightarrow{H_2PtCl_6} (C_6H_5)_2Si(CH_2CH_2CH_2OOCCH_3)_2 \xrightarrow{HCl}$$

$$(C_6H_5)_2Si(CH_2CH_2CH_2OH)_2 \xrightarrow[C_5H_5N]{CH_3C_6H_4SO_2Cl} (C_6H_5)_2Si(CH_2CH_2CH_2OSO_2C_6H_4CH_3)_2$$

$$\xrightarrow[DMSO]{LiBr} (C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$$

The starting material diphenylsilane was prepared by the reduction of commercial dichlorodiphenylsilane with lithium aluminum hydride in ether solvents (Table 8). Work-up consisted of replacing the ether with hydrocarbon solvent to precipitate aluminum salts, washing the organic layer with ice water, and distilling the product.

The previously used hydrosilylation procedure, with diphenylsilane, allyl acetate and chloroplatinic acid, gave inconsistent results (Table 9). The adduct was hydrolyzed to the alcohol without isolation because the alcohol is a solid. NMR yield estimates as high as 60% were obtained, but NMR cannot be used to distinguish between monosubstituted and disubstituted silane units. Chromatography was necessary to give sufficiently pure material for crystallization. The use of allyl alcohol or allyl bromide instead of the acetate, and the use of benzoyl peroxide as the catalyst were also unsatisfactory. A more satisfactory method involved the use of $[(C_6H_5)_3P]_3RhCl$ as the catalyst and $CH_2{=}CHCH_2OSi(CH_3)_3$. This method was used in runs 11-14. Yields by NMR were in the 70-85% range, and the products were sufficiently pure that they could be crystallized without undergoing

Table 8. Diphenylsilane

Run No.	Moles $(C_6H_5)_2SiCl_2$*	Solvent	Yield (grams)	Yield (percent)
1	0.1	n-butyl ether	9.2	50
2	1	"	129	70
3	4	tetrahydrofuran	352	48
4	0.4	ethyl ether	54.5	74
5	7	"	670	52
6	7	"	992	77
7	7	"	1030	80
8	14	"	1855	72
9	14	"	1060	80

* A 10-15% excess of $LiAlH_4$ was used

Table 9. Reactions of Diphenylsilane with $CH_2=CHCH_2OCOCH_3$ and with $CH_2=CHCH_2OSi(CH_3)_3$

Run No.	Moles $(C_6H_5)_2SiH_2$	Catalyst	Allyl Substituent	Isolated Yield $(C_6H_5)_2Si(CH_2CH_2CH_2OH)_2$ g	%
1	0.27	H_2PtCl_4	$OCOCH_3$	8.1	10
2	0.3	"	"	9	10
3	0.1	"	"	12	40
4	0.07	"	"	8.4	40
5	0.277	"	"	25	30
6	0.1	"	"	12	40
7	0.54	"	"	16.2	10
8	0.71	"	"	30	14
9	1.0	"	"	0	0
10	0.2	"	"	24	40
11	0.1	$[(C_6H_5)_3P]_3RhCl$	$OSi(CH_3)_3$	21.3	71
12	0.4	"	"	36	30
13	1.0	"	"	174	58
14	1.5	"	"	248	55
15	5	"	"	1090	73
16	5.5	"	"	940	57
17	3	"	"	504	56
18	7.5	"	"	832	37
19	8.15	"	"	1660	68

column chromatography. Isolated yields were 55-73%. A side reaction caused by the rhodium catalyst is rearrangement of the double bond of the olefin. In run 18 the allyl compound was added very slowly in an attempt to minimize this rearrangement. NMR indicated 70% addition and only a 37% yield of alcohol was subsequently crystallized. In run 19 the allyl compound was added rapidly; NMR indicated 84% addition and a 68% yield of alcohol was crystallized.

The alcohol was converted to the dibromide via the toluenesulfonate by the same method used for the methylsilanes above:

$$(C_6H_5)_2Si(CH_2CH_2CH_2OH)_2 + CH_3\text{-}C_6H_4\text{-}SO_2Cl \xrightarrow{\text{Pyridine}} (C_6H_5)_2Si(CH_2CH_2CH_2OSO_2\text{-}C_6H_4\text{-}CH_3)_2$$

$$\xrightarrow[\text{DMSO}]{\text{NaBr}} (C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$$

Runs 1-10 of Table 10 were carried out in this way. The toluenesulfonate could not be crystallized and was therefore not isolated. Yields based on NMR spectra were consistently 80-90%. The dibromide in most of the runs could not be crystallized, and the product of runs 1-3 and 6-14 were obtained as 90-95% pure liquids by solvent partition. In runs 4, 5, and 10 the DMSO solution was used directly in the following step. The reaction of the alcohol with PBr_3 was also investigated, and in early studies a reaction temperature of 80° resulted in dephenylation. With ether as a solvent and a reaction period of 3 days at room temperature, yields to 81% were obtained. Run 15 gave crystalline product for the first time.

The reaction of the dibromide with sodium nitrite was conducted in DMSO, and conversion of bromide units to nitro were in the range of 50 to 65%, based on NMR data. Statistically, the incidence of two of the desired nitro groups in a molecule should be the square of the NMR yield, and the isolated yields of dinitro

Table 10. Bis-(3-bromopropyl)diphenylsilane

Run No.	Moles $(C_6H_5)_2Si(CH_2CH_2CH_2OH)_2$	Yield $(C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$ g	%
1	0.04	11.4	67
2	0.068	17.4	60
3	0.053	15.1	67
4	0.367		*
5	0.285		*
6	0.677	138	56
7	3.0	1099	86
8	0.44	124	66
9	2.9	889	72
10	0.73		*
11	0.1	21.3	50
12	0.3	99.7	78
13	2.44	842	81
14	2.54	822	76
15	4.96	1415	67**

* Not isolated, used in subsequent step

** Recrystallized yield

compound (Table 11) are in this range, as high as 34%. The use of impure starting material results in large losses on recrystallizing the product, and the highest yields - runs 9 and 11 - were obtained with recrystallized dibromide.

The oxidative nitration of $(C_6H_5)_2Si(CH_2CH_2CH_2NO_2)_2$ to give $(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{\underset{|}{\overset{|}{CH}}}})_2$ is summarized in Table 12. Conversions based on NMR data were 60-70%, but isolated yields of recrystallized product were only 21 to 38%. This step is expected to be particularly amenable to improvements as a result of process studies.

Attempts were made to fluorinate the potassium salt of this gem dinitro compound with elemental fluorine, but only traces of product were obtained. Perchloryl fluoride, however, was found to give high yields of $(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{\underset{|}{\overset{|}{CF}}}})_2$ after a suitable solvent was found, an equal mixture of water, methanol and dimethyl sulfoxide. Yield of 60 to 86% of recrystallized product were obtained (Table 13), and the lower yields are attributed to impurities in the starting material.

Attempts to dephenylate $(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{\underset{|}{\overset{|}{CF}}}})_2$ with bromine under the conditions used with $(C_6H_5)_2Si(CH_3)CH_2CH_2CF(NO_2)_2$ did not give promising results. Not more than 60% of the phenyl groups could be cleaved. It appears that a combination of the electron-withdrawing and steric effects of a second fluorodinitropropyl group is sufficient to render impractical the replacement of the two phenyl groups by bromine. It was found, however, that if water is added to the bromination mixture after the initial reaction has run its course, consumption of bromine becomes rapid. Methylene chloride and acetic acid were used as solvents.

Table 11. Bis-(3-nitropropyl)diphenylsilane

Run No.	$(BrCH_2CH_2CH_2)_2Si(C_6H_5)_2$ moles	$(C_6H_5)_2Si(CH_2CH_2CH_2NO_2)$ isolated yield g	%
1	0.033	2.4	20
2	0.035	3	24
3	0.317	19.3	17
4	0.645	53.1	23
5	2.6	233	25
6	0.29	15.5	15
7	2.1	98	13
8	0.235	22	26
9	0.054	6.6	34
10	4.73	423	25
11	1.7	201	33

Table 12. Bis-(3,3-dinitropropyl)diphenylsilane

Run No.	$(C_6H_5)_2Si(CH_2CH_2CH_2NO_2)_2$ moles	$(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{CH}})_2$ isolated yield g	%
1	0.69	83	27
2	0.28	32.6	26
3	0.067	11.1	37
4	0.5	67.2	30
5	0.05	47	21
6	0.5	49.3	22
7	0.204	34.7	38
8	0.403	63	35

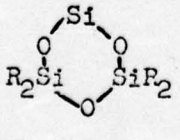
Table 13. Bis-(3-fluoro-3,3-dinitropropyl)diphenylsilane

Run No.	$(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{CH}})_2$ moles	$(C_6H_5)_2Si(CH_2CH_2\underset{NO_2}{\overset{NO_2}{CF}})_2$ isolated yield g	%
1	0.154	44.7	60
2	0.13	36.5	58
3	0.05	19.8	82
4	0.1	35.3	73
5	0.089	36.6	85
6	0.085	35.4	86
7	0.132	39.0	61

A crystalline solid was obtained that was identified as the cyclic trisiloxane. The compound was identified by elemental analysis and its molecular weight determined by vapor osmometry was 1030; theoretical for trimer is 1036. The compound melted without decomposition at 207-9°C, and a sample heated at 215° did not change in molecular weight. Attempts to polymerize this thermally stable solid are in progress.

The accelerating effect of water on the dephenylation is rationalized on the basis of the hydrolysis of the initially formed phenyl bromosilane. The resulting silanol or its ether is dephenylated more readily than the bromosilane.

$$(C_6H_5)_2SiR_2 \xrightarrow{Br_2} C_6H_5SiBrR_2 \xrightarrow[Br_2]{H_2O} C_6H_5\underset{OH}{SiR_2} \longrightarrow Br\underset{OH}{SiR_2} \xrightarrow{-HBr}$$



R= $CH_2CH_2\underset{NO_2}{\overset{NO_2}{CF}}$

Polymerization Studies. Published[2] siloxane polymerization studies are concerned mainly with the dimethylsiloxane system, and the most often used starting material is dimethyldichlorosilane. Generally, silicones are produced in two steps. Dimethyldichlorosilane is hydrolyzed to cyclic oligomers, consisting of 3 to 5 units, which are purified by distillation and then polymerized using catalysts. With some catalysts, however, the dimethyldichlorosilane can be polymerized directly. Table 14 surveys the effect of various conditions on this hydrolytic polymerization reaction.[2] Methods of this general type were examined for the hydrolysis of (3-fluoro-3,3-dinitropropyl)methyldibromosilane, although the steric and electron-withdrawing effects of the nitro-containing substituent were not expected to facilitate the reaction.

Experiments dealing with the polymerization of this dibromide and related difluorides are summarized in Table 15. The experiments were conducted on 1 g samples. Agitation was provided by magnetic stirring or mechanical shaking. Molecular weights were determined by vapor phase osmometry. Acids, bases and heavy metallic oxides were used as catalysts. In the initial experiments, the acid catalyst was HBr, produced by hydrolyses of the dibromosilane and ether was used as a solvent. The products were cyclic oligomers (runs 1-3) with an average of 4 units. Elemental analysis showed that the materials were in fact cyclic.

In that this oligomer was the first polysiloxane prepared containing fluorodinitroalkyl group, its thermal stability was of particular interest. The DTA and TGA curves, obtained at the Naval Weapons Center[12] are shown in Fig. 1. The DTA showed exotherm onset at 215° with a peak at 240°. This high thermal stability of the oligomer encouraged further polymerization studies aimed at higher molecular weight linear polysiloxanes with the properties of rubbers.

Figure 1. DTA and TGA

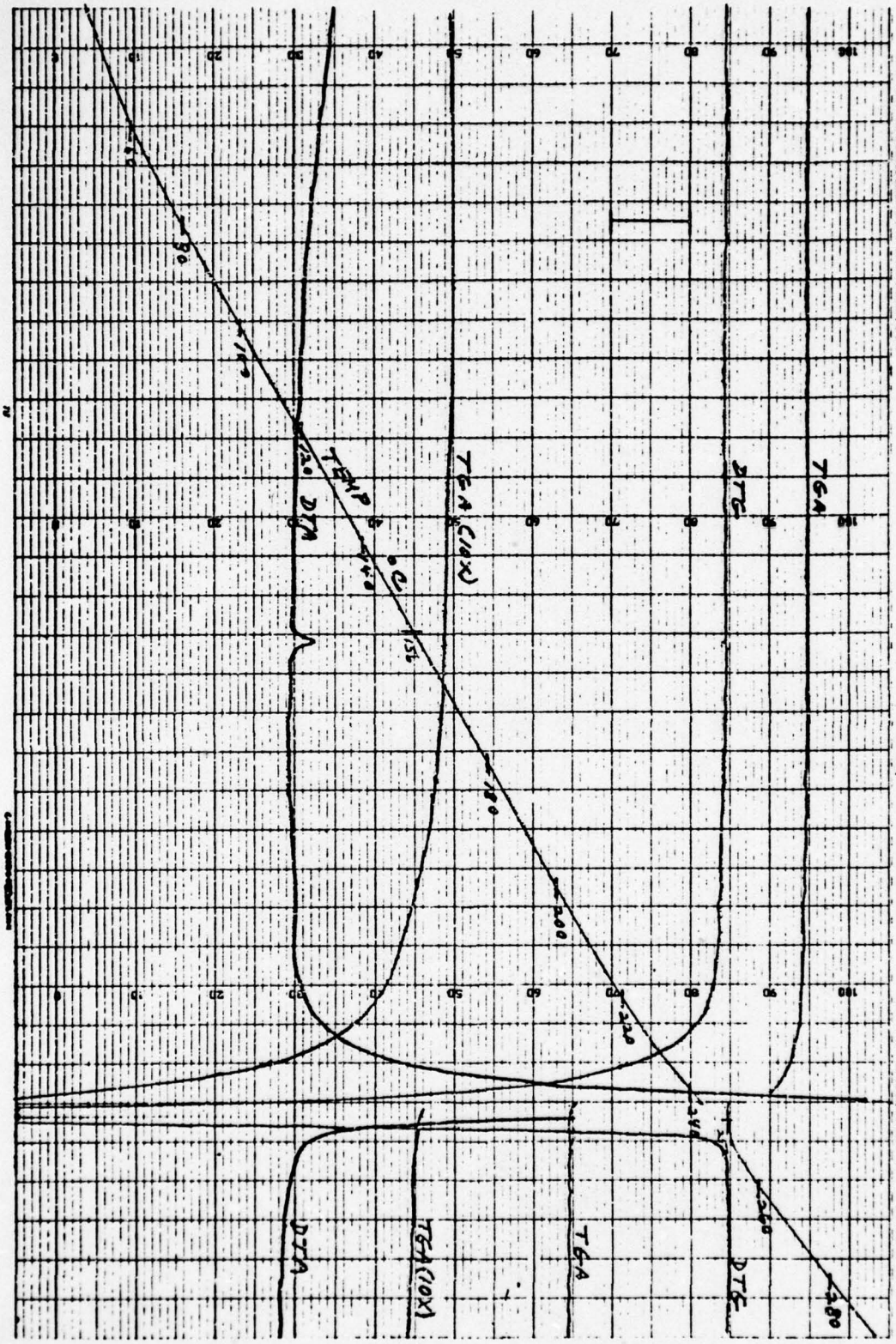


Table 14. Reported Dimethylsilicone Preparations

Method No.	Silane*	Conditions of hydrolysis	Result	Ref. No.
1	A	Water	Cyclic Polymers and polydimethyl-siloxane-α,ω-diols	
2	A	Salt Hydrates	Mainly higher polymers	3
3	A	Concentrate HCl	Mainly lower polymers	
4	A	50-85% Sulfuric acid	Mainly higher polymers	4
5	A	Excess of alkali	" " "	5, 6
6	A	Water and ammonia, pH6.5-8.5	Tetramethyldisiloxane-1,3-diol	
7	A	Water and Water-miscible solvents	Mainly cyclic lower polymers	7, 8
8	A	Water and diethylether	" " " "	9a,b,c
9	A	Deficiency of water, dioxane and ether	Linear α,ω-dichlorosiloxanes	5
10	A	Alcohol and carboxylic acid	Mainly higher polymers	8
11	B,C	Water, free of acid and base	Dimethylsilanediol	9c
12	C	Deficiency of water	α,2-diethoxysiloxanes	

* A = $(CH_3)_2SiCl_2$; B = $(CH_3)_2Si(OCH_3)_2$; C = $(CH_3)_2Si(OCH_2CH_3)_2$

Table 15. Polymerizations of Fluorodinitropropylmethyldihalosilanes

Run No.	Halosilane*	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
1	A	Et_2O-ice	HBr	0	0.5	776	3.7
2	"	" "	"	"	"	834	4.0
3	"	" $-H_2O$	"	20	0.25	850	4.0
4	"	Atmospheric moisture	"	"	18	935	4.5
5	"	H_2O, 0.25 mol CH_3SiCl_3	",HCl	"	2	1540	-
6	"	Skellysolve F-H_2O	"	"	0.5	888	4.2
7	"	CH_2Cl_2-H_2O	"	"	0.5	552	2.6
8	"	Acetone-H_2O	"	"	"	1024	4.9
9	"	Acetone-CH_2Cl_2,0.5 eq H_2O	"	"	2	939	4.5
10	"	" " "	"	"	16	900	"
11	"	" " ,excess H_2O	"	"	72	899	4.3
12	"	t-butanol	"	70	1.5	856	4.1
13	"	CH_3COOH-MeOH	"	20	2.5	848	4.0
14	"	" "	"	"	168	806	3.8
15	"	$Na_2SO_4 \cdot 2.4H_2O$	"	"	120	1005	4.8
16	"	$Na_2SO_4 \cdot 7H_2O$	"	"	"	1102	5.2
17	"	$CuCl_2 \cdot 2H_2O$	"	"	48	984	4.7
18	"	75% H_2SO_4	H_2SO_4	"	1	1191	5.7
19	"	" "	"	"	17	1144	5.4
20	"	30% $SO_3 \cdot H_2SO_4$	"	"	72	1195	5.7
21	"	95% EtOH	Concd HCl	78	8	1104	5.3
22	"	1 mol MeOH	$FeCl_3 \cdot 6H_2O$	180	2	1176	5.6
23	"	" "	$FeCl_3$	100	1	1000	4.8

Table 15 (cont'd.)

Run No.	Halo-silane *	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
24	"	1 mol $PhMe_2SiOEt$	$FeCl_3$	150	96	1713	-
25	"	Et_2O-H_2O	28% NH_4OH	0	0.5	809	3.9
26	"	" -Dioxane	"	20	"	832	4.0
27	"	" -H_2O	$NaHCO_3$	"	"	815	3.9
28	"	PhMe, -H_2O	K_2CO_3	100	1.5	1167	5.6
29	"	CCl_4-H_2O	"	20	72	904	4.3
30	"	5 N KOH, 0.5 mol $MeSiCl_3$	KOH	20	0.5	986	-
31	"	C_6H_6, 0.25 mol $MeSiCl_3$	K_2CO_3	20	16	1051	-
32	B	CH_2Cl_2	NaOH	"	24	900	4.3
33	"	20% EtOH	"	"	0.3	1286	6.1
34	"	90% EtOH	NaOAc	"	15	914	4.4
35	C	-	CsOH	100	120	868	4.1
36	"	H_2O	"	20	4	1101	5.2
37	"	"	K_2CO_3	"	11	1080	5.1
38	"	"	$NaHCO_3$	"	12	981	4.7
39	"	"	Et_3N	"	12	789	3.8
40	"	95% EtOH	TlOOCH	"	14	877	4.2
41	"	80% EtOH	NaOAc	"	"	1024	4.9
42	"	1) NaOMe, 2) H_2SO_4, 3) MeOH/KOH	KOH	"	20	990	4.7
43	A	MgO	$HgCl_2$, CH_3CN	100	96	1076	5.1
44	"	CaO	"	"	"	924	4.4
45	"	Pb_3O_4	$CuCl_2$, CH_3CN	"	84	907	4.3
46	C	CaO	-	"	120	N.R.	-

Table 15 (cont'd.)

Run No.	Halo-silane*	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
47	A	Skellysolve F, Ag_2O	$CuCl_2$, CH_3CN	50	12	N.R.	-
48	"	" , CuO	-	"	22	"	-
49	"	" , ZnO	-	"	"	"	-
50	B	CH_2Cl_2, CaO	-	20	72	938	4.5
51	"	" , PbO	-	"	216	982	4.7
52	"	" , Cu_2O	-	"	"	N.R.	-
53	C	" , CaO	-	"	120	"	-

* A = $Br_2CH_3SiCH_2CH_2CF(NO_2)_2$

B = $F_2CH_3SiCH_2CH_2CF(NO_2)_2$

C = $\left[(NO_2)_2CCH_2CH_2SiFCH_3\right]_2O$

Run 4 (Table 15) represents an attempt to hydrolyze the neat dibromide slowly by exposure to atmospheric moisture. The product, however, was similar to that obtained with ether. The use of a hydrocarbon solvent (run 6) or methylene chloride (run 7) also failed to give higher polymer. The latter, however, gave the trimer, of significance in later polymerization studies. In runs 8-11, acetone, in which both water and the silane are soluble, was used as the solvent. Variations in the amount of water used, and stepwise hydrolysis gave no significant change. Similar results were obtained with t-butanol or a mixture of methanol and acetic acid (runs 12-14).

Salt hydrates have been reported to give high polymers by providing a heterogeneous reaction surface. The use of hydrated sodium sulfate on cuprous chloride in this work, however, gave products with an average of five units per molecule (runs 15-17).

The use of 75% sulfuric acid as the reaction medium, reported to give high polymers with dimethylsilicones, was also investigated. A 5.7 unit polymer was obtained (run 18). A similar product was obtained with 30% fuming sulfuric acid (run 20) and with concentrated HCl in refluxing ethanol (run 21).

Papetti and others[11] have used ferric chloride and its hydrate to polymerize siloxy carboranes to resins and elastomers. Therefore the dibromosilane was reacted with one equivalent of methanol to form the methoxybromosilane. After addition of the ferric chloride catalysts, polymers of 4.8 to 5.6 units was obtained (runs 22-23). Copolymerization of dibromosilane and phenyldimethylethoxysilane under the same conditions produced a substance with a molecular weight of 1713.

The hydrolysis of the dibromide was also carried out under basic conditions (runs 25-31) and oligomers of 4-6 units were obtained. Ammonium hydroxide, sodium bicarbonate, potassium carbonate and potassium hydroxide were used as reagents and ether, dioxane, water, toluene and carbon tetrachloride as solvents.

Fluorosilanes differ in reactivity from other halosilanes in that they are not hydrolyzed readily under neutral or acidic conditions, but are reactive toward base. This selectivity offers possibilities for the preparation of polymers. The hydrolysis of $CH_3SiF_2CH_2CH_2CF(NO_2)_2$ with sodium hydroxide in the presence of methylene chloride gave a 4.3 unit product (run 32), but in 20% aqueous ethanol, a 6.1 unit product was obtained (run 33). The hydrolysis of

the difluorodisiloxane, $(NO_2)_2CFCH_2CH_2SiF(CH_3)OSiF(CH_3)CH_2CH_2CF(NO_2)_2$, was examined under weakly basic conditions in the hope that hydrolysis would take place more slowly than condensation of the resulting hydroxysilanes. In this way intermolecular condensation would be favored over intramolecular condensation. The products (runs 37-41) generally contained 4-5 monomer units. An attempt to hydrolyze only one end of the dimer with a small amount of base followed by acid condensation (run 42) was also unsuccessful. The polymerization of unreactive halosiloxanes, such as $(CF_3C_6H_4)_2SiCl_2$, with metal oxides[12] has been reported. Calcium, magnesium, zinc, lead and copper oxide can be used with acetonitrile and cupric or mercuric chlorides as catalysts. Application of this method to the bromo and fluoro silanes gave low molecular weight products (runs 43-46). The metallic oxides have also been used in inert solvents[13], but no advantage was obtained with the nitro compounds (runs 47-53).

Studies aimed at the preparation of higher polymers from (3-fluoro-3,3-dinitropropyl)methyl siloxane oligomers are summarized in Table 16. Silicone oligomers used commercially for polymerization are generally purified by distillation. This example, however, was not sufficiently volatile for distillation, and the properties of the trimer, tetramer, and pentamer did not differ sufficiently for separation by column chromatography or selective solvent precipitation. Consequently, the product mixtures obtained by hydrolysis of the halides were used without fractionation.

Initially, thermal polymerization without the use of catalysts was investigated (runs 1-2). Hydrolysis of the dibromide was carried out under conditions that yield mainly trimer. Heating the product for 24 hrs at 150° and 180° gave materials with 3.7 and 6.8 monomer units per mole respectively. In runs 3-20,

Table 16. Polymerization of (3-fluoro-3,3-dinitropropyl)methylsiloxane oligomers

Run No.	Hydrolysis Conditions	Starting MW	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
1	D	-	-	-	150	24	799	3.7
2	"	-	-	-	180	24	1418	6.8
3	A	1183	Et_2O	H_2SO_4	20	24	1194	5.7
4	"	1194	-	"	"	144	1280	6.1
5	"	776	-	"	"	120	1000	4.8
6	"	834	-	"	90	16	1104	5.3
7	"	776	0.05 mol $(CH_3)_6Si_2O$	"	20	120	955	4
8	"	1000	-	20% $SO_3 \cdot H_2SO_4$	20	216	1180	5.6
9	"	"	-	"	100	24	1192	5.7
10	"	"	-	30% $SO_3 \cdot H_2SO_4$	20	72	840	4.0
11	B	"	H_2SO_4-H_2O	75% H_2SO_4	20	2	1462	7.0
12	"	1100	" "	90% H_2SO_4	"	"	1243	5.9
13	"	"	" "	85% H_2SO_4	"	"	1167	5.6
14	"	"	" "	80% H_2SO_4	"	"	1173	5.6
15	"	"	" "	70% H_2SO_4	"	"	1233	5.9
16	"	"	" "	65% H_2SO_4	"	"	1099	5.2
17	"	"	" "	60% H_2SO_4	"	"	1000	4.8
18	"	"	" "	55% H_2SO_4	"	"	1201	5.7
19	"	"	" "	50% H_2SO_4	"	"	1123	5.3
20	"	"	" "	45% H_2SO_4	"	"	1144	5.4
21	A	834	-	CF_3SO_3H	80	8.5	1208	5.8
22	"	1000	-	$BF_3 \cdot Et_2O$	20	22	1116	5.3

Table 16 (cont'd.)

Run No.	Hydrolysis Conditions	Starting MW	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
23	A	1000	H_2SO_4-H_2O	48% HF	20	24	911	4.3
24	"	"	-	$SnCl_4$	"	552	938	4.5
25	"	"	-	$AlCl_3$	"	"	889	4.2
26	"	"	-	48% HI	"	"	908	4.3
27	"	"	-	P_2O_5	"	"	963	4.6
28	"	840	-	$FeCl_3$ $C_6H_5CH_3$, CF_3COOH	"	120	988	4.7
29	"	834	-	NaOH	90	12	1081	5.1
30	"	1000	-	"	150	0.5	1219	5.8
31	"	1462	-	Et_3N	85	48	1372	6.5
32	"	850	-	NaOH	150	0.25	976	4.6
33	"	"	-	"	"	0.5	973	4.6
34	"	"	-	"	"	0.75	980	4.7
35	"	"	-	"	"	1	1051	5.0
36	"	"	-	"	"	3	1026	4.9
37	"	"	-	"	"	5	1118	5.3
38	"	"	-	"	"	7	1095	5.2
39	"	"	-	"	"	24	1069	5.1
40	C	-	-	NaOH	150	0.5	1698	8.1
41	"	-	-	"	"	"	1452	6.9
42	"	-	-	"	"	1	1414	6.7
43	"	-	-	"	"	4	2000	9.5

Table 16 (cont'd.)

Run No.	Hydrolysis Conditions	Starting MW	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
44	C	850	H_2SO_4-H_2O	NaOH	150	24	2222	10.6
45	"	-	-	"	"	72	2019	9.6
46	"	-	-	"	"	96	2040	9.6
47	"	-	-	KOH	"	0.5	1118	5.3
48	"	-	-	"	"	4	1350	6.4
49	"	-	-	"	"	24	1100	5.2
50	"	-	-	$(CH_3)_3SiONa$	"	0.5	1792	8.5
51	"	-	-	"	"	4	1627	7.7
52	"	-	-	"	"	24	1483	7.1
53	"	-	-	$(CH_3)_4NOSi(CH_3)_3$	"	0.5	1016	4.8
54	"	-	-	"	"	4	1019	4.9
55	"	-	-	"	"	24	1396	6.6
56	"	-	-	NaH	"	4.5	1229	5.9
57	"	-	-	"	"	7	1442	6.9
58	"	-	-	"	"	23	1740	8.3
59	"	-	-	"	"	48	1778	8.5
60	"	-	-	"	"	120	1743	8.33
61	"	-	-	"	"	1	1438	6.8
62	"	-	-	"	"	72	2347	11.2
63	"	-	-	"	"	96	2322	11.2
64	"	2322	added additional catalyst	"	"	24	1258	6.0
65	"	-	(1) Cat/150° (2) Et_2O wash	"	-	120	3111	14.8

Table 16 (cont'd.)

Run No.	Hydrolysis Conditions	Starting MW	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
66	E	-	-	NaH	150	24	959	4.6
67	F	-	-	"	"	"	924	4.4
68	G	-	-	"	"	"	993	4.7
69	H	-	-	"	"	"	1526	7.3
70	I	-	-	"	"	"	1208	5.8
71	J	-	-	"	"	"	1625	7.7
72	"	1625	Et_2O wash	-	20	96	2037	9.7
73	D	-	-	NaH	150	24	1780	8.5
74	"	-	-	"	"	42	1313	6.3
75	"	1313	added additional catalyst	"	"	72	1072	5.1
76	"	1313	Et_2O wash	-	20	96	3000	14.3
77	"	1418	-	NaH	180	96	1409	6.7
78	"	552	-	"	150	40	2269	10.8
79	"	2269	Et_2O wash	-	20	96	3105	14.8
80	"	-	-	NaH	150	108	2197	10.5
81	"	2197	Et_2O extraction	-	40	16	2507	11.9
82	"	-	-	$(n\text{-}bu)_3N$	150	24	919	4.4
83	"	-	-	Quinoline	"	"	1210	5.8
84	"	-	-	Biguanide	100	"	874	4.2
85	"	-	-	Pyridine	"	"	885	4.2
86	"	-	-	NaH	150	72	2231	10.6
87	D	-	1.0 mole $(C_6H_5)_2Si(O\text{-})_2$	"	"	"	2322	-

Table 16 (cont'd.)

Run No.	Hydrolysis Conditions	Starting MW	Solvents and Reagents	Catalyst	Temp °C	Time hrs	Polymer MW	Polymer Units
88	D	2197	0.1 mole $(C_6H_5)_2Si(O-)_2$	NaH	150	24	1171	-
89	"	-	0.5 mol $C_6H_5(CH_3)_2SiO-$	"	"	96	1299	-
90	"	-	1.0 mol $C_6H_5Si(O-)_3$	"	"	72	4074	-
91	"	-	0.1 mol $C_6H_5Si(O-)_3$	"	"	2	1160	-
92	"	-	" "	"	"	27	1507	-
93	"	1507	Et_2O wash	-	20	16	1635	-
94	"	-	0.2 mol $C_6H_5Si(O-)_3$	NaH	150	24	1722	-
95	A	911	-	$(C_6H_5COO)_2$	100	30	1710	8.1
96	"	1710	Et_2O wash	-	20	96	2600	12.4
97	D	1684	-	$(C_6H_5COO)_2$	100	48	1641	7.8
98	"	1641	Et_2O wash	-	20	24	2800	13.3
99	A	911	-	$(C_4H_9OO)_2$	150	30	947	4.5

1. This column refers to the reagents used to produce the starting polysiloxane from the dibromosilane.

A. Ethyl ether-water
B.i) Ethyl ether-water ii) dissolved in conc. sulfuric acid
C. Water
D. Methylene chloride-water
E. Conc. sulfuric acid
F. 75% Sulfuric acid
G. 50% Aqueous ethanol
H. Acetone-water
I. Carbon tetrachloride-potassium carbonate-water
J. Skellysolve F-water
K. Methylene chloride- 1N NaOH

catalysis by sulfuric acid was studied. In run 3, the polymer was treated with sulfuric acid in ether solution, and the molecular weight was essentially unchanged. Subsequently no solvent was used (runs 4-6), and variations in time (16 to 144 hrs) and temperature (20° to 90°) resulted in only small increases in molecular weight. The addition of hexamethyldisiloxane (run 7) did not affect the reaction, and the use of fuming sulfuric did not give significant increases in molecular weight (runs 8-10). In runs 11-20, the oligomer was dissolved in concentrated sulfuric acid, and sufficient water was then added to give the acid concentrations shown. Significant increases were not obtained. Other proton and Lewis acids were also tried without success (runs 21-28).

Base catalysis of the polymerization of the cyclic oligomers was also studied. Initially, the oligomer was obtained by the hydrolysis of the dibromide in the presence of ether, conditions that generally give product averaging four units per mole. Only small molecular weight increases were observed on heating this material with sodium hydroxide or triethylamine (runs 29-39). Subsequently, it was found that the method of hydrolysis of the dibromide influences greatly the ease of the base-catalyzed polymerization. Higher polymers were obtained when the initial dibromide hydrolysis was carried out in the absence of organic solvents or in the presence of methylene chloride, shown previously to give mainly trimer. Heating this material with powdered sodium hydroxide at 150° was found to give a molecular weight maximum in 24 hrs of 10.6 monomer units (run 44). Potassium hydroxide (runs 47-49), sodium trimethylsilanate (runs 50-52), and tetramethylammonium trimethylsilanate (runs 53-55) also catalyzed the reaction but not as effectively as sodium hydroxide. Sodium hydride (runs 56-63) was found to be as effective as sodium hydroxide and is preferred because of the ease with which small

quantities can be manipulated. Hydrocarbon solvent (runs 71-73) for the bromide hydrolysis gave results similar to methylene chloride, but sulfuric acid, aqueous ethanol, acetone and carbon tetrachloride (runs 66-70) were not as satisfactory. Organic bases (runs 82-85) did not function successfully as catalysts with oligomers that were polymerized with NaOH or NaH.

Higher molecular weight polymer fractions were found to be insoluble in ether, and extraction of materials with molecular weights of 1600 to 2000 in this way gave products with molecular weights to over 3,000 (runs 65, 72, 76, 79, 81, 96, and 152). Heating polymer samples with additional catalyst resulted in a decrease in molecular weight (runs 64, 75).

The results of the base-catalyzed polymerization studies are consistent with the function of the cyclic trimer as the active component of the oligomer mixtures. A similar effect has been reported for the polymerization of trifluoropropylmethylsiloxanes[14f].

The copolymerization of $FC(NO_2)_2CH_2CH_2SiBrCH_3$ with $(C_6H_5)_2SiCl_2$ and with $C_6H_5SiCl_3$ was studied briefly (runs 87-94). An equimolar amount of the latter gave a product with a molecular weight of 4074.

A method by which commercial silicones are crosslinked is hydrogen abstraction by free radical initiators. This method was explored with the nitro-containing materials (runs 95-99) using benzoyl peroxide, and in one case (run 95) a doubling of molecular weight was observed. This method may be useful with high molecular weight linear polysiloxanes.

Phosphazenes. High molecular weight linear poly(dialkoxyphosphazenes), $\left(\begin{matrix}R\\P=N\\R\end{matrix}\right)_n$, are noted for their excellent thermal stability and low glass transition

temperatures.[15] Examples with fluorinated substituents have been reported[16] with glass transition temperatures as low as -68°. Similar polymers with nitro substituents would be expected to provide useful explosives. Attempts were therefore made to prepare poly[bis(fluorodinitroethoxy)phosphazene].

The method generally used to synthesize materials of this type is to heat a suspension of the alkoxide salt with a solution of poly(dichlorophosphazene) in an inert solvent such as benzene. This method cannot be used with fluorodinitroethanol because the alkoxide is unstable. Pyridine has been used as the solvent and acid acceptor to promote the reaction of fluorodinitroethanol with dichlorophosphazene cyclic trimer and tetramer on another program[17] at Fluorochem. The same conditions were therefore examined using linear poly(dichlorophosphazene).

The linear poly(dichlorophosphazene) was prepared by a published procedure[18], consisting of heating the cyclic trimer at 250° until the material was viscous at this temperature. The polymer was separated from unreacted trimer by precipitation from benzene and hexane. The reaction of the polymer with an excess of fluorodinitroethanol was carried out in pyridine solution, with a reaction period of 2-5 days at 0-25°. Dark solid polymeric products were obtained by washing the reaction mixtures with water and with hydrochloric acid. Quantitative NMR analyses of the products showed as high as 72% by weight of fluorodinitroethoxy groups, but all samples showed substantial amounts of pyridine groups. The pyridine groups were bound to the polymer backbone and could not be removed by acid washing.

III. EXPERIMENTAL

Allyloxytrimethylsilane. Over a 1.5 hr period, ammonia was passed through a rapidly stirred solution (ice bath cooling) of 348 g (6.00 mol) of allyl alcohol and 3 liters of methylene chloride while 652 g (6.00 mol) of chlorotrimethylsilane was introduced below the surface of the liquid. The mixture was filtered and the cake of ammonium chloride was dissolved in 1 liter of water. The methylene chloride layer (~750 ml) that separated was dried with magnesium sulfate and was added to the filtrate. The methylene chloride solution was distilled to give 546 g (70%) of allyloxytrimethylsilane:[19] bp 96-101°; d_4^{20} = 0.793; NMR (neat) δ5.9 (m, 1 H, -CH=), 5.2 (m, 2 H, $=CH_2$), 4.0 (m, 2 H, CH_2O), 0.0 (s, 9 H, $(CH_3)_3Si$).

(3-Hydroxypropyl)methyldiphenylsilane. Allyloxytrimethylsilane (1162 g, 8.94 mol) was added dropwise to a solution of 1539 g (7.77 mol) of methyldiphenylsilane and 80 mg of chlorotris(triphenylphosphine)rhodium at 130° over a 3 hr period. The reaction solution was added dropwise with stirring, over a 1.5 hr period, to a solution of 3 liters of methanol and 800 ml of 1 N hydrochloric acid. The mixture was stirred overnight, and an equal volume of water was added. The aqueous solution was extracted with 3 liters of methylene chloride. The combined methylene chloride solution was washed with water and with saturated salt solution and was dried with sodium sulfate. The solvent was removed by distillation to give 1950 g (98%) of crude (3-hydroxypropyl)methyldiphenylsilane; physical data was reported previously.[1]

(3-p-Toluenesulfonatopropyl)methyldiphenylsilane. Toluenesulfonyl chloride (1597 g, 8.38 mol) and then 766 ml (9.53 mol) of pyridine were added to a solution of 1950 g (7.62 mol) of crude (3-hydroxypropyl)methyldiphenylsilane in 1950 ml of methylene chloride at 4°C. The mixture was stirred overnight and was poured into

water. The methylene chloride layer was separated and the aqueous layer was extracted once with methylene chloride. The combined methylene chloride solution was washed with water, with 1 N hydrochloric acid and with saturated salt solution and was then dried with sodium sulfate. Most of the solvent was removed by distillation. The product was cyrstallized from 1200 ml of ethyl ether and 1200 ml of Skellysolve F to give 1925 g (62%) of (3-p-toluenesulfonatopropyl)-methyldiphenylsilane; physical was was reported previously.[1]

(3-Nitropropyl)methyldiphenylsilane. A solution of 206 g (2.00 mol) of sodium bromide and 410 g (1.00 mol) of (3-p-toluenesulfonatopropyl)methyldiphenylsilane in 1.5 liters of dimethyl sulfoxide was stirred at ambient temperature overnight. Sodium nitrite (276 g, 4.00 mol) was added and the reaction temperature was kept below 35° by means of a cooling bath. After 95 min the product was isolated to give 171 g of material containing 131 g (46%) of (3-nitropropyl)methyldiphenylsilane; physical data was reported previously.[1]

(3-3-Dinitropropyl)methyldiphenylsilane. A solution of 95 g (0.333 mol) of (3-nitropropyl)methyldiphenylsilane in 600 ml of methanol was added to a solution of 14.7 g (0.367 mol) of sodium hydroxide in 80 ml of distilled water at 0°C. After 15 min the cold solution was mixed with 23.0 g (0.333 mol) of sodium nitrite in 80 ml distilled water. The solution was quickly poured into a cold (0°C) rapidly stirred mixture of 113 g (0.667 mol) of silver nitrate in 800 ml of distilled water and 600 ml of ethyl ether. The mixture was stirred for 1 hr at 0° and 1 hr at room temperature. The mixture was allowed to settle for 5 min. Then the solution was filtered and the silver was washed with ether. The layers were separated and the aqueous solution was extracted twice with ether. The combined ether solutions were washed three times with saturated sodium chloride

solution and were evaporated to yield 154 g of material containing 104 g (68.5%) of (3,3-dinitropropyl)methyldiphenylsilane: physical data was reported previously.[1]

(3-Fluoro-3,3-dinitropropyl)methylsiloxane. A solution of 11.5 g (0.0325 mol) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane in 60 ml of methylene chloride was added dropwise with stirring to 60 ml of water. After 30 min, the layers were separated and the aqueous solution was extracted with methylene chloride. The combined organic fraction was washed with water and with saturated salt solution and was dried over sodium sulfate. After the solvent was evaporated, the residue was heated to 150°C and 10 mg of sodium hydride was added remotely. The mixture was heated 42 hrs at 150°. The products showed a molecular weight of 1313 by vapor phase osmometry in 1,3-dichloroethane. Twice, the oil was shaken for 24 hr periods with 50 ml of ethyl ether and the ether was discarded. After the sample was dried at 130° for 4 days, a molecular weight of 3000 was found. The material, d_4^{24} 1.38, was soluble in methylene chloride, 1,2-dichloroethane, and acetone, slightly soluble in chloroform, and insoluble in ether, benzene, hexane, water cyclohexane and carbon tetrachloride.

(3-Fluoro-3,3-dinitropropyl)methyldifluorosilane. Poly(3-fluoro-3,3-dinitropropyl)methylsiloxane (13.5 g, 64.3 mmol of monomer) was dissolved in 50 ml of ethanol, 25 ml of 48% hydrogen fluoride and 15 ml of water. The mixture was agitated for 24 hrs and was then diluted with water. The product was extracted with methylene chloride, and the methylene chloride solution was washed with water and with saturated salt solution, and was dried over sodium sulfate. The solvent was evaporated and the residue was distilled to give 12 g

(80%) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane: bp 67° (3 mm); NMR ($CDCl_3$) δ 0.4 (t, J=6 Hz, 3 H, CH_3Si), 0.9 (m, 2 H, CH_2Si) and 2.9 (m, 2 H, $CH_2CF(NO_2)_2$; fluorine NMR ($CDCl_3$) ϕ 104.5 (t, J=16 Hz, 1 F, $F(NO_2)_2C$ and 132.3 (sextet, J=6 Hz, 2 F, SiF_2); IR (film) 1600, 1435, 1370, 1325, 1275, 1220, 1190, 1065, 1025, 930, 910, 870, 860, 830, and 805 cm^{-1}.

Anal. Calcd for $C_4H_7F_3N_2O_4Si$: C, 20.69; H, 3.02; H, 12.07. Found: C, 20.67; H, 2.88; N, 12.52.

A mixture of 33 g (0.0932 mol) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane and 15.7 g (0.373 mol) of sodium fluoride was dissolved in 100 ml of ethanol, 25 ml of 48% hydrogen fluoride and 15 ml of water with agitation. After 3 days, the mixture was poured into water and was extracted twice with methylene chloride. The organic solution was washed with water and with saturated salt solution and was dried over sodium sulfate. The solvent was evaporated and the residue was distilled to give 17.8 g (82%) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane.

Bromine (113 ml, 2.07 mol) was added to 180 g of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane (ice bath cooling) and the solution was heated at 70° at 18 mm to remove bromine and phenyl bromide. The distillation was continued to give impure (3-fluoro-3,3-dinitropropyl)methyldibromosilane. The distillate was dissolved in 150 ml of methylene chloride and was poured over 400 ml of ice and water. After 30 min, the layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic solution was washed with water and with saturated salt solution, and was evaporated. The residue was heated to 180°/0.2 mm to remove dibromobenzene isomers. The material was agitated with 200 ml of ethanol and 50 ml of 48% hydrogen

fluoride for 4 days. The solution was poured into water and was extracted with methylene chloride. The solution was washed with water and with saturated salt solution, and was dried with sodium sulfate. After the solvent was evaporated, the residue was distilled to give 80.8 g (67%) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane (bp 75°, 7 mm) and 6.4 g (6%) of 1,3-bis-(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane (bp 156°/0.2 mm).

(3-Fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane. A solution of 5.4 g (0.1 mol) of sodium methoxide in 30 ml of dry methanol was added dropwise to 23.2 g (0.1 mol) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane with ice bath cooling. After 0.5 hr, the methanol was evaporated and the residue was distilled at 79-85° (3 mm) to give a mixture of starting material (20%), dimer (18%) and product (62%). The yield of (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane was 13.9 g (57%) by NMR. A sample was purified by gas chromatography: NMR($CDCl_3$) δ 0.3 (d, J=6 Hz, 3 H, CH_3Si), 0.8 (m, 2 H, CH_2Si), 2.8 (m, 2 H, $CH_2C(NO_2)_2F$) and 3.5 (s, 3 H, CH_3OSi); fluorine NMR($CDCl_3$) ϕ 104.7 (t, J=16 Hz, 1 F, $CF(NO_2)_2$ and 138.1 (sextet, J=6 Hz, 1 F, FSi); IR (film) 1600, 1440, 1375, 1330, 1275, 1215, 1195, 1100, 1065, 1030, 915, 880, 855, 835, and 810 cm^{-1}.

1,3-Bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane. A solution of 1.25 g (5.12 mmol) of impure (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane in 25 ml of methanol, 5 ml of water and 1 ml of concentrated sulfuric acid was stirred for 20 hrs. The solution was poured into water and extracted with methylene chloride. The solution was washed with water and with saturated salt solution, and was dried with sodium sulfate. The solvent was evaporated and the residue was distilled to give 0.7 g (62%) of 1,3-bis-(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane: bp 158° (0.200 mm);

NMR (neat) δ 0.3 (d, J=6 Hz, 6 H, CH_3Si), 0.9 (m, 4 H, CH_2Si) and 2.9 (m, 4 H, CH_2CF); fluorine NMR (neat) ϕ 105.5 (t, J=20 Hz, 2 F, $FC(NO_2)$) and 132.0 (sextet, J=6 Hz, 2 F, FSi); IR (film) 1590, 1435, 1365, 1320, 1235, 1100, 1025, 970, 910, 875, 855, 820, 800, 880 cm^{-1}.

Anal. Calcd for $C_8H_{14}F_4N_4O_9Si_2$: C, 21.72; H, 3.17; N, 12.67. Found: C, 21.88; H, 3.05; N, 13.50.

A solution of 6.6 g (0.123 mol) of sodium methoxide in 42 ml of dry methanol was added dropwise to 40.5 g (0.175 mol) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane at 0°. After 0.5 hr, the methanol was evaporated and the residue was distilled (7 mm/80°C) to dryness to give a mixture containing starting material (26%) dimer (11%) and product (63%). The mixture was redistilled through a 4 inch vigroux column and the fractions boiling from 71-79°/3 mm were collected. The end fraction showed only 13% of the dimer. The distillate was dissolved in 250 ml of methanol, 50 ml of water and 10 ml of concentrated sulfuric acid and was stirred for 2 hrs. The mixture was poured into water and extracted with methylene chloride. The solution was washed with water and with saturated salt solution and was dried with sodium sulfate. The solvent was evaporated and the residue was distilled to give 7.7 g (20%) of starting material and 10.7 g (29%) of 1,3-bis-(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane.

Bis-(3-hydroxypropyl)diphenylsilane. A mixture of 1500 g (7.33 mol) of 90% diphenylsilane, 0.1 g of chlorotris(triphenylphosphine)rhodium (I) and 200 g of allyloxytrimethylsilane was heated to 100°. Heating was stopped and the pot temperature rose to 120°. Additional allyoxytrimethylsilane, a total of 2800 g (21.6 mol), was added at a rate sufficient to maintain reflux. This

solution was added to a solution of 15 ml of concentrated HCl and 600 ml of water in 3 liters of methanol. After 24 hrs the product was extracted with methylene chloride. Crystallization from methylene chloride and Skelly F yielded 1500 g (68% yield) of bis-(3-hydroxypropyl)diphenylsilane.

Bis-(3-bromopropyl)diphenylsilane. Bis-(3-hydroxypropyl)diphenylsilane, 1490 g (4.96 mol) was added to a solution of 1043 g (3.86 mol) of phosphorous tribromide in 3 l of ether, which was maintained at room temperature by a water bath. The mixture was stirred for 72 hrs, and then was added to ice. The product was extracted with water, dried, stripped of solvent and extracted into Skelly F, giving 1683 g of semicrystalline, 90% pure, bis-(3-bromopropyl(diphenylsilane. Recrystallization from ethanol gave 1400 g, (67%), of pure bromide, mp 48-9°.

Anal. Calcd for $C_{18}H_{22}Br_2Si$: C, 50.72; H, 5.20. Found: C, 50.74; H, 5.17.

Bis-(3,3-dinitropropyl)diphenylsilane. Bis-(3-nitropropyl)diphenylsilane (73 g, 0.204 mol), was added to 33 g (0.5 mol) of potassium hydroxide in 50 ml of water and 250 ml of methanol. When solution was complete, 200 ml water and 34.5 g (0.5 mol) of sodium nitrite were added. This solution was quickly added to an ice bath cooled mixture of 170 g silver nitrate (1 mol) in 300 ml water and 500 ml of ether. After the mixture was stirred at room temperature for 2 hrs, 200 ml saturated sodium chloride solution was added. The silver precipitate was filtered, and the solution made slightly acidic with acetic acid. The ether layer was separated, washed, dried and stripped. The product was crystallized from ethylene chloride and Skelly F, giving 34.5 g (38% yield) of bis-(3,3-dinitropropyl)diphenylsilane, mp 96-7°; NMR ($CDCl_3$), δ 7.40 (s, 10 H, C_6H_5), 6.01 (t, J=7 Hz, 2 H, $CH-(NO_2)_2$), 2.4 (m, 4 H, $\underline{CH_2}-CH_2Si$) and 1.2 (m,

4 H, CH_2Si), IR($CHCl_3$) 1570, 1330 and 1120 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}N_4O_8Si$: C, 48.21; H, 4.50; N, 12.49. Found: C, 48.32 H, 4.59 N, 12.29.

Bis-(3-fluoro-3,3-dinitropropyl)diphenylsilane. Perchloryl fluoride was bubbled into a vigorously stirred solution of 40 g of bis-(3,3-dinitropropyl)-diphenylsilane (0.009 mol) and 13.2 g of potassium hydroxide (0.2 mol) in 150 ml water, 200 ml methanol and 200 ml of dimethyl formamide at room temperature. When gas uptake stopped, water was slowly added and the product precipitated out. Filtration yielded 42 g of a light tan solid. Recrystallization gave 36.6 g, (85% yield), of white crystalline product, mp 85-6°, IR (KBr) 1590, 1430, 1320, 1260, 1200, 1100 and 700 cm^{-1}: proton NMR ($CDCl_3$) δ 7.35 (s, 10 H, C_6H_5), 2.63 (m, 4 H, CH_2CH_2Si), 1.17 (m, 4 H, CH_2Si); fluorine NMR($CDCl_3$) ϕ 105.7 (J_{HF}=18 Hz).

Anal. Calcd for $C_{18}H_{18}O_8N_4F_2Si$: C, 44.63; H, 3.75, N, 11.57. Found: C, 44.84; H, 3.85 N, 11.39.

1,1,3,3,5,5-Hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane. A solution of 10 g (.021 mol) of bis-(3,3,3-fluorodinitropropyl)diphenylsilane in 25 ml of methylene chloride and 25 ml of acetic acid was stirred with 10 g (.0625 mol) bromine for 3 days. Water (10 ml) was added and the reaction mixture was stirred for 24 hours. The solution was washed with water and solvent was removed. The product was redissolved in methylene chloride and 2 g of bromine was added. Crystals slowly formed and after 4 days, 4.8 g (67% yield) of 1,1,3,3,5,5-hexakis-(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane was isolated by filtration. The product was recrystallized from ethyl acetate and Skelly F to give white crystals, mp 207-9°, density > 1.59 g/cc; IR (KBr) 1590, 1320, 1270, 1210, 1090 cm^{-1}; proton NMR (D_6 acetone) δ 3.14 (m, 4 H, CH_2-CF), 1.20 (m, 4 H, CH_2Si); fluorine NMR

(D_6acetone) ϕ 106.0; molecular weight (vapor phase osmometer/EtOAc), 1010 ± 5% (trimer = 1038).

Anal. Calcd for $C_6H_8N_4O_9F_2Si$: C, 20.83; H, 2.33, N, 16.19. Found: C, 21.00; H, 2.36 N, 16.17.

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